Some notes on functional differentiation

(a physicist's perspective)

Motivation from DFT

Suppose we want to minimise the density functional $E[n]$ for electron densities, where

$$n(\bar{r}) \geq 0 \qquad \int d\bar{r}\, n(\bar{r}) = N \tag{1}$$

where N is the particle number. When taking functional derivatives, we say that $n_0(\bar{r})$ is a minimising density whenever

$$\left.\frac{\delta E}{\delta n(\bar{r})}\right|_{n_0(\bar{r})} = 0 \tag{2}$$

but what does (2) really mean?

If $n_0(\bar{r})$ is the minimising solution then

$$E[n_0 + \epsilon h] \geq E[n_0] \tag{3}$$

for any density $n_0 + \epsilon h = n(\bar{r})$

For this we need the conditions $n(r) = n_0 + \epsilon h \geq 0$ and

$$N = \int d\bar{r}\,(n_0 + \epsilon h) = \int n_0\, d\bar{r} + \epsilon \int h(\bar{r})\, d\bar{r}$$

$$= N + \epsilon \int h(\bar{r})\, d\bar{r} \quad \Rightarrow \quad 0 = \int d\bar{r}\, h(\bar{r}) \tag{4}$$

Therefore the density variation $h(\bar{r})$ must integrate to zero.

Let us define $$f(\epsilon) = E[n_0 + \epsilon h] \qquad (5)$$

Then (3) implies that

$$f(\epsilon) \geq f(0) \qquad \forall \epsilon$$

and therefore that $f(\epsilon)$ has a minimum at $\epsilon = 0$. Since $f(\epsilon)$ is an ordinary real function we can use the standard rules of calculus and require

$$\left.\frac{df}{d\epsilon}\right|_{\epsilon=0} = 0 \qquad (6)$$

(provided that $f(\epsilon)$ is differentiable which we tacitly assume).
Eq. (6) is equivalent to

$$0 = \left.\frac{df}{d\epsilon}\right|_{\epsilon=0} = \lim_{\epsilon\to 0} \frac{f(\epsilon) - f(0)}{\epsilon}$$

$$= \lim_{\epsilon\to 0} \frac{E[n_0 + \epsilon h] - E[n_0]}{\epsilon} \qquad (7)$$

This expression motivates the following definition for the functional derivative.

Let $A[n]$ be a functional of $n(\vec{r})$; then we define the Gateaux derivative at $n(\cdot)$ by

$$dA(n;h) = \lim_{\epsilon\to 0} \frac{A[n+\epsilon h] - A[n]}{\epsilon} \qquad (8)$$

If you like to know more about this you can check the entry "Gateaux derivative" on Wikipedia.

In the particular case (common in DFT and in physics in general) that $dA(n;h)$ can be written in the form

$$dA(n;h) = \int d\bar{r}\; a(\bar{r})\, h(\bar{r}) \qquad (9)$$

then we call

$$a(\bar{r}) = \frac{\delta A}{\delta n(\bar{r})} \qquad (10)$$

the functional derivative. Note that, while (9) is unique, the function $a(\bar{r})$ need not be.

In density functional theory, where we have condition (4) on the density variations, it follows that

$$\int d\bar{r}\,\big(a(\bar{r}) + c\big)\, h(\bar{r}) = \int d\bar{r}\; a(\bar{r}) + c \underbrace{\int d\bar{r}\; h(\bar{r})}_{0}$$

$$= \int d\bar{r}\; a(\bar{r})$$

and therefore

$$a(\bar{r}) \text{ modulo a constant} = \frac{\delta A}{\delta n(\bar{r})} \qquad (10)$$

Let us now give some explicit examples.

We take a general functional of the form

$$A[n] = \int d\bar{r}\; \mathcal{L}(n, \nabla n) \qquad (11)$$

where

$\mathcal{L}(x, \vec{y})$ is a function of x, $\vec{y} = (y_1, y_2, y_3)$

which we take to be smooth and differentiable.

Let us now calculate the Gateaux derivative:

$$dA(n;h) = \lim_{\epsilon\to 0} \frac{A[n+\epsilon h] - A[n]}{\epsilon}$$

$$= \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left\{ \int d\bar{r}\, \mathcal{L}(n+\epsilon h, \nabla n + \epsilon \nabla h) - \int d\bar{r}\, \mathcal{L}(n, \nabla n)\right\} \quad (12)$$

If $\vec{r} = (r_1, r_2, r_3)$ and $\partial_j = \frac{\partial}{\partial r_j}$ we introduce the notation

$$\delta x = h(\bar{r}) \quad , \quad \delta y_j = \partial_j h(\bar{r})$$

so that

$$dA(n;h) = \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left\{ \int d\bar{r}\left(\mathcal{L}(x+\epsilon\delta x, \bar{y} + \epsilon \delta \bar{y}) - \mathcal{L}(x,\bar{y})\right)\Big|_{n,\nabla n}\right\}$$

$$= \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left\{ \int d\bar{r}\left(\epsilon \frac{\partial \mathcal{L}}{\partial x}\Big|_{n,\nabla n} \delta x + \sum_j \epsilon \frac{\partial \mathcal{L}}{\partial y_j}\Big|_{n,\nabla n} \delta y_j + O(\epsilon^2)\right)\right\}$$

$$= \lim_{\epsilon\to 0} \int d\bar{r}\left(\frac{\partial \mathcal{L}}{\partial x}\Big|_{n,\nabla n} \delta x + \sum_j \frac{\partial \mathcal{L}}{\partial y_j}\Big|_{n,\nabla n} \delta y_j\right) + O(\epsilon)$$

$$= \int d\bar{r}\left\{ \frac{\partial \mathcal{L}}{\partial x}\Big|_{n,\nabla n} h(\bar{r}) + \sum_j \frac{\partial \mathcal{L}}{\partial y_j}\Big|_{n,\nabla n} \partial_j h(\bar{r})\right\} \quad (13)$$

We now suppose that $h(\bar{r})$ vanishes at the boundaries of our spatial domain then we can perform a partial integration of the second term of the integrand in Eq. (13).

We thus obtain:

$$dA(n;h) = \int d\bar{r} \left\{ \frac{\partial \mathcal{L}}{\partial x}\Big|_{n,\nabla n} - \sum_j \partial_j \left(\frac{\partial \mathcal{L}}{\partial y_j} \right)\Big|_{n,\nabla n} \right\} h(\bar{r})$$

$$= \int d\bar{r}\; a(\bar{r})\, h(\bar{r}) \qquad (14)$$

from which we can identify

$$a(\bar{r}) = \frac{\partial \mathcal{L}}{\partial x}\Big|_{n,\nabla n} - \sum_j \partial_j \left(\frac{\partial \mathcal{L}}{\partial y_j} \right)\Big|_{n,\nabla n} \qquad (15)$$

This expression is sometimes written as

$$a(\bar{r}) = \frac{\partial \mathcal{L}}{\partial n(\bar{r})} - \nabla \cdot \frac{\partial \mathcal{L}}{\partial \nabla n(\bar{r})} \qquad (16)$$

with the more precise meaning given by eq. (15).

Let us apply (15) to some functionals used in DFT. We take the functional for the exchange energy

$$E_x^{LDA}[n] = C \int d\bar{r}\; n^{4/3}(\bar{r}) \qquad (17)$$

where LDA stands for Local Density Approximation.

In this case $\mathcal{L}(x,\vec{y}) = C x^{4/3}$

and, therefore

$$a(\vec{r}) = \left.\frac{\partial \mathcal{L}}{\partial x}\right|_{n,\nabla n} = \left.\frac{4}{3} C x^{1/3}\right|_{n,\nabla n} = \frac{4}{3} n(\vec{r})^{1/3} C$$

So we obtain

$$v_x^{LDA}(\vec{r}) = \frac{\delta E_x^{LDA}}{\delta n(\vec{r})} = \frac{4}{3} C\, n^{1/3}(\vec{r}) \qquad (18)$$

which is the LDA exchange potential.

Let us now take a bit more elaborate case. The Gradient Expansion Approximation correction to the LDA functional is given by

$$E_x^{GEA}[n] = \alpha \int d\vec{r}\, \frac{(\nabla n)^2}{n^{4/3}} \qquad (19)$$

In this case: $\mathcal{L}(x,\vec{y}) = \alpha \frac{\vec{y}^2}{x^{4/3}}$

and consequently

$$a(\vec{r}) = \left.\frac{\partial \mathcal{L}}{\partial x}\right|_{n,\nabla n} - \sum_j \partial_j \left(\left.\frac{\partial \mathcal{L}}{\partial y_j}\right|_{n,\nabla n}\right)$$

$$= -\alpha \frac{4}{3} \left.\frac{\vec{y}^2}{x^{7/3}}\right|_{n,\nabla n} - \sum_j \partial_j \left(\left.\frac{2 y_j}{x^{4/3}} \alpha\right|_{n,\nabla n}\right)$$

$$= -\frac{4}{3}\alpha \frac{(\nabla n)^2}{n^{7/3}} - \sum_j \partial_j \left(\frac{2\alpha\, \partial_j n}{n^{4/3}}\right)$$

$$= -\frac{4}{3}\alpha\frac{(\nabla n)^2}{n^{7/3}} - \sum_j 2\alpha\frac{\partial_j^2 n}{n^{4/3}} + \frac{8}{3}\alpha\sum_j\frac{\partial_j n\,\partial_j n}{n^{7/3}}$$

$$= \frac{4}{3}\alpha\frac{(\nabla n)^2}{n^{7/3}} - 2\alpha\frac{\nabla^2 n}{n^{4/3}}$$

and we therefore obtain that

$$v_x^{GEA}(\vec{r}) = \frac{\delta E_x^{GEA}}{\delta n(\vec{r})} = \frac{4}{3}\alpha\frac{(\nabla n)^2}{n^{7/3}} - 2\alpha\frac{\nabla^2 n}{n^{4/3}} \qquad (20)$$

The potentials in (18) and (20) are defined up to a constant as a consequence of Eq. (10). This reflects the physical condition that potentials are always defined up to a gauge.

Almost all functional derivatives in DFT are calculated according to the steps above. It would be useful to get some experience in this by trying some expressions for yourself.